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Fracture Toughness and Micro-Strain of Y-TZP Nanoceramics at Different Sintering Temperature

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Abstract

The objective of this research is to study the effect of sintering temperature on the mechanical properties and micro-strain of yttria tetragonal zirconia polycrystalls (Y-TZP) nanostructure. Where green disk formed by uniaxially press, sintered at (1500 – 1550 – 1600°C) in air for 2hr then polished to mirror shape for fracture toughness and micro-hardness measurement by Vickers indenter at (60 kg to 100gm) loads. Atomic force microscopy (AFM) technique was use to measure the change in grain size and shape of the samples, X-ray diffraction (XRD) evaluated to identify the phases and to measure the micro-strain of the samples.

The Results show that increasing sintering temperature will increase the grain size with increasing the average of micro-strain. Tetragonal phase is the prevailing phase with small amount of cubic phase and the amount of monoclinic phase was under detection limite after sintering but there is increas in lattice dimension according to micro-strain calculation and grinding process produce micro-strain. With increasing the sintering temperature micro-hardness and fracture toughness will increas.
Keywords: Zirconia; polycrystalls; Nanostructure; Porosity; Sintering; Micro-strain

الخلاصه:-

الهدف من هذا البحث هو دراسة تاثير درجة حرارة التلبيد على الخواص الميكانيكية و الانفعال المرن للزركونيا المثبتة باليتريا النانوية. حيث تم تلبيد العينات المكبوسة عند درجات (1500 – 1550 – 1600م^0) في الهواء لمدة ساعتين ، ثم بعد التلبيد تم صقلها لغرض اجراء فحص الصلادة المايكروية و لفحص متانة الكسر بواسطة جهاز فكرز (من 60 كغم الى 100غم). تم استخدام جهاز المجهر الذري لايجاد التغير في حجم و شكل الحبيبات في العينات ، و تم فحصها بواسطة الاشعة السينية لتحديد نوع الطور الناتج و لتحديد قيمة الانفعال المايكروي للعينات.

لقد بينت النتائج انه عند زيادة درجة التلبيد سوف يزداد الحجم الحبيبي مع زيادة الانفعال المايكروي. ان الطور السائد الناتج بعد التلبيد هو الطورالرباعي ، مع زيادة ابعاد المشبك نتيجة للانفعال المرن ، و مع زيادة درجة التلبيد تزداد الصلادة المايكروية مع زيادة متانة الكسر.

الكلمات المفتاحية : زركونيا ، متعدد البلورات ، التركيب النانوي ، المسامات ، التلبيد ، الانفعال المايكروي.

1 –Introduction

Zirconia has been considered as a suitable choice for dental restorations due to its good mechanical properties, tooth-colored and natural appearance and low plaque accumulation. This material is a non-cytotoxic metal oxide, insoluble in water and has no potential of bacterial adhesion. In addition, it has radio-opacity properties and exhibits low corrosion (Khamv and Moshiri, 2012). It was introduced 20 years ago to solve the problem of alumina brittleness and the consequent potential failure of implants. Biomedical grade zirconia exhibits the best mechanical properties of oxide ceramics: this is the consequence of phase transformation toughening, which increases its crack propagation resistance (Jerome Chevalier, 2006). Zirconia exhibit three well defined polymorphs (Stevens, 1986):

$$\text{Monoclinic} \xleftrightarrow{1170^{\circ}C} \text{Tetragonal} \xleftrightarrow{2370^{\circ}C} \text{Cubic} \xleftrightarrow{2680^{\circ}C} \text{Liquid}$$

Gravie, Hannink & Pasco in publishing their seminal article "ceramic steel" were first to realized the potential of Zirconia for increasing both the strength and toughness of ceramic by utilizing the (t→m) transformation of metastable (t) particle induced by the presses of stress field a head of the crack. The volume change and shear strain developed in martensitic reaction were organized as opposing the opening of the crack and therefore acting to increase the resistance of ceramic to crack

propagation (Stevens, 1986). Tetragonal-to-monoclinic phase transformation in Zirconia can be induced by stress, temperature and surface treatments (Mccolm and Leonard, 1983).

The goal of the sintering process of advanced ceramic materials is most frequently to obtain a material with a high relative density and homogeneous microstructure consisting of small grains. It is well known that the sintering behavior and final grain size are influenced, in particular, by the size of the particles of input ceramic material, the degree of its agglomeration, and also by the microstructure of green body, which in addition to the properties of powder material is also determined by the shaping technology used(Karel *et.al.*, 2010).

After heat (sintering) and mechanical (grinding) treatment, this will produce stress concentration in the samples and then to the strain in the microstructure (micro-strain). The effect of heat and mechanical stress on the microstructure of yttria stabilized zirconia have been studded in this research by XRD, where the change in d-lattice spacing of the samples were investigated before and after sintering and grinding process, where zirconia Are the most stress-affected substances, and if the stresses are high enough this will lead to phase transformation from (t→m) with cracks and finally the product failur. So, by studying XRD charts in this research its possible to know the effect of grinding and sintering on the material stability and the amount of change in its dimensions(Yusheng and Jianzhong, 2008).

2 – Material and Methods

2 – 1 Preparation of Samples

Commercially Yttria Stabilized Zirconia powder [FIXANAL, SIGMA ALDRICH, GERMANY] was used (90.082% ZrO_2 - 5.452%Y_2O_3) having grain size between (80 to 130nm) and (5.947g/cm^3) density. The powder is milled in mill balls for an hour to remove agglomeration then uniaxially pressed to obtain the green body have 16 mm in diameter and 3.5±0.04 mm in thickness at 250 Mpa for 2 min with addition of PVA as binder material for easy handling. The green sample was sintered for 2hr in air at (1500 – 1550 – and 1600^{o}C) with heating and cooling rate (10^{o}C/min). XRD test was made before and after sintering to characterize if there any phase transformation (t→m) occur where the monoclinic phase before sintering was (0%) and the present phase is (100%) tetragonal phase. AFM test was made to detect the shape and size of YSZ samples before and after sintering. After that the samples grind and polish to a mirror surface for Vickers measurement.

2 – 2 Physical Tests:-

1- **Microstructure -** For microscope examination wet grind was used with Sic as a grinding paper [in grad 220, 400, 600, 1000, 1500, 2000] and water as cooling liquid and for marking grain boundary HF acid was used for the sample after grinding with 90% HF concentration and 10% distilled water, then polished to mirror surface.

2-**Density -** The true density of the specimens was determined according to the Archimedes principle after sintering and the value of theoretical density of powder has been found from the x – ray examination equal to 5.947gm/cm^3.

$$\text{Apparent density} = [Wd/ (Wd-Wi)] \times \rho_w \quad (1)$$

$$\text{Body density} = [Wd/ (Ws-Wi)] \times \rho_w \quad (2)$$

Where Wd- dry weight (gm), Wi- Immersion weight (gm), Ws- saturated weight (gm), ρ_w- water density (gm/cm³)(Malaysian standard, 2003).

3 – Porosity - The porosity of the sample after sintering can be found from the equations:-

True porosity (T.P) = [(T.D-B.D)/ (T.D)]*100% (3)

Where B.D – density of sintered sample, T.D- theoretical density of sintered sample (Manual of weighing application, 1999).

4 – Shrinkage - the shrinkage in diameter and thickness of the samples were measured by electronic farina after and before the sintering stage and according to the following equation the percent of shrinkage can be found:

$$SH\ \%=[(D_o-D_1)/D_o]*100 \quad (4)$$

$$SH\ \%=[(t_o-t_1)/t_o]*100 \quad (5)$$

D_1= diameter after sintering, D_o= diameter before sintering in (mm), t_o = thickness before sintering (mm), t_1 = thickness after sintering (mm)

(جنان ستار خشان،2001)

2- 3 Mechanical Tests:-

Vickers hardness and fracture toughness of the as-sintered specimens were determined using the indentation technique**.**

1-**Fracture Toughness-** the indentation fracture toughness was measured using a Vickers macro-hardness tester (Zwick & Co. KG.Einsingen bei Ulm Z323) with a load of 3, 2, 1 kg. This load was selected after making indents with the loads from 60 to 5 kg on the as-sintered specimen**.** The crack length was measured by using an optical microscope. The equation was the well-known formula (Evans and Charles, 1976) (Enrique Rocha-Rangel**):**

K_{IC} = 0.16 (c/a)$^{-1.5}$(H√a) (6)

H = 1.8544 × (P/a^2)

K_{IC} = Fracture toughness (MPa·$m^{0.5}$)

H = Vickers hardness (MPa)

P = Test load in Vickers hardener (MPa)

c = Average length of the cracks obtained in the tips of the Vickers marks (microns)

a = Half average length of the diagonal of the Vickers marks (microns).

2 – Micro-Hardness - and the indentation hardness were measured using a Vickers micro-hardness tester (Digital Micro Vickers Hardness Tester TH714) with a load of 100 gm in holding time (15s). The equation is (ASM International, 2000) :

$$H.V=1.8544\ (P/d_{av}{}^2) \quad (7)$$

P=load (N or Kgf), d_{av} =indent diagonal length (mm).

2 – 4 Structural Tests:-

1 – XRD - Cu K (40 kV, 30 mA) XRD (Lab XRD-6000, shimad ZU X-ray diffraction) was used for phase identification and calculation of the relative phase content of monoclinic and tetragonal ZrO_2. Surfaces of each specimen were analyzed from 25 to 35° with a step size of 0.02° for 0.4s. Identify the phase quantity according to toraya et al, the following equation was used:-

Xm=[Im(hkl)+Im(hkl)]/[Im(hkl)+Im(hkl)+It(hkl)] (8)

Where Xm - mol fraction of m-phase, Im-area under curve of m-phase (Caroline Cotesa and others, 2014). In every stage of sample manufacture (as powder, sintered sample, grind, mechanical test) it's examined by XRD.

2 – **Micro-Strain -** microscopic strain and stress derived from diffraction peak-width changes during loading, unloading and heating(Yusheng and Jianzhong, 2008).

$$\varepsilon = [\Delta d/d] = [(d-d_o)/d_o] \quad (9)$$

3 – AFM - AFM examination was used to study structure & grain size, with following data: AA3000 SPM system.

3 – Results:-

3 – 1 Uniaxially Pressing and Sintering:-

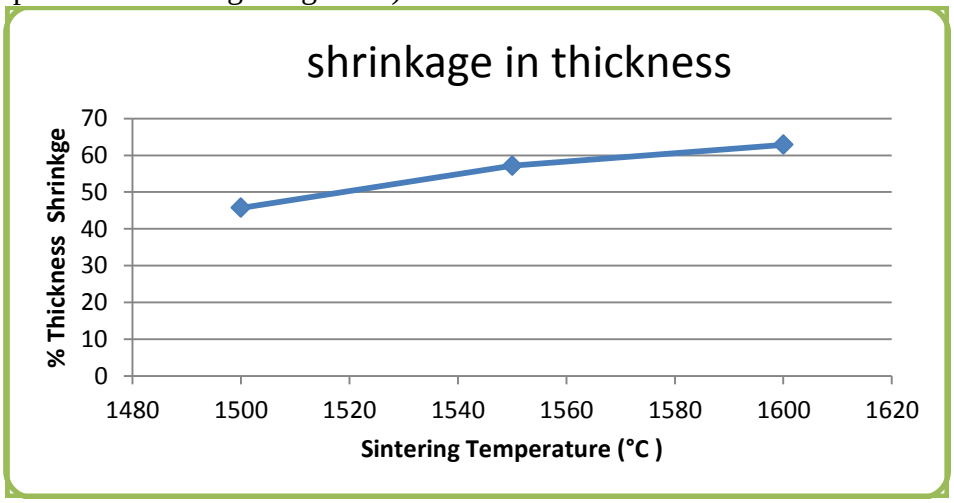
Uniaxially Pressing - after many experiment to choose the best pressing load suitable to sample dimension that will not lead to high stress concentration and crack formation during sintering, the (5 ton) load was the best load between (5 – 10 – 15 ton), its observed that with increasing pressing load then pore number and size will decreas and during sintering crack will increas due to increas in grain size so that there is no space to expand the internal grains. To avoid samples collapse during handling binder material added, at 200 to 500^{0}C this material will be evaporated and its place will be occupy be growth grain during sintering.

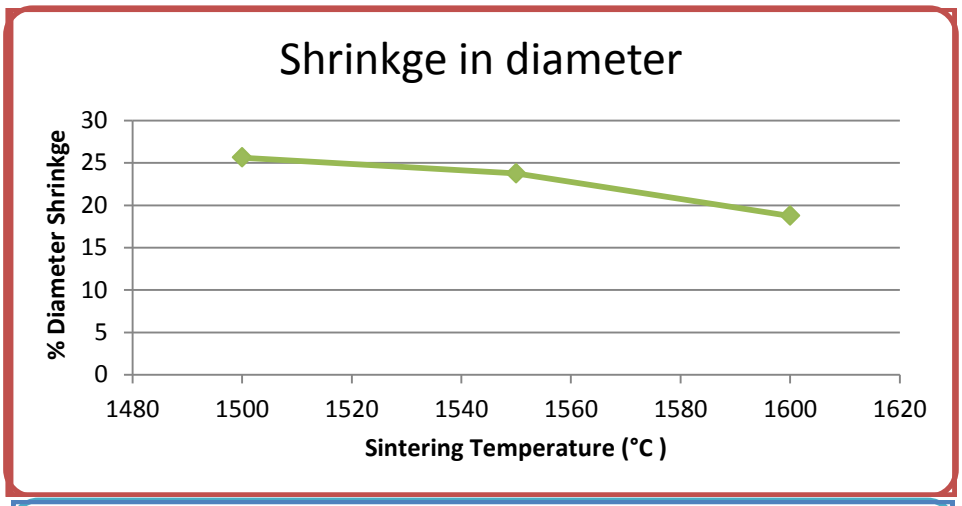
Sintering- many experiments has made to choose suitable sintering time for all sintering temperature that produce samples have good physical and mechanical properties. Where experiments of this work and based on the results of many research show that the best sintering time is (2hr), and heating and cooling rate equal to 10^{0}C/min (the sintering time and heating rate has been deduced after many experiment to choose the best rate that produced dense samples without cracking and less porosity percent, with taking into account the experiment and result of the other researchers). The resulted samples have good grain growth, high density and good mechanical properties with tetragonal phase (the dominant phase).

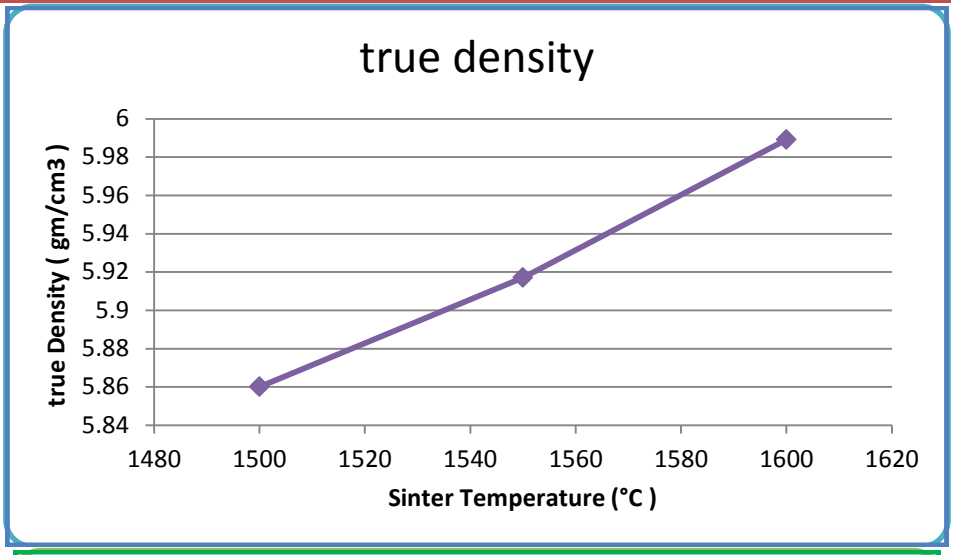
3 – 2 Physical Test Results:-

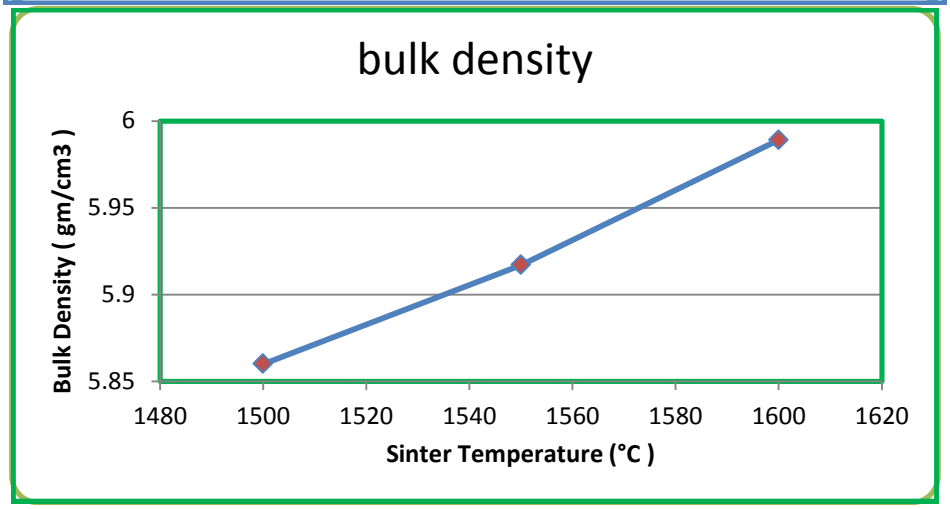
1 – density - Sintering at 1500- 1550 – 1600^{0}C with suitable sintering time and pressing load produced samples have density ≈ 97.491% of standard theoretical density, where the density increas with increase sintering temperature and this will produce in porosity percent (≈ 0.790% % at 1600^{0}C) as shown in the figure(1).

2 – **Shrinkage -** Increas sintering temperature will increas the shrinkage percent in sample thickness from 45.7% to 62.8%, and reduce the shrinkage percent in sample diameter from 25.6% to 18.7% (this may be due to grain growth that will occupy porosity area, this obvious on the samples because there were no cracks on sample surface after grain growth).




Shrinkge in diameter
% Diameter Shrinkge
30
25
20
15
10
5
0
1480
1500
1520
1540
1560
1580
1600
1620
Sintering Temperature (°C)


true density
true Density (gm/cm3)
6
5.98
5.96
5.94
5.92
5.9
5.88
5.86
5.84
1480
1500
1520
1540
1560
1580
1600
1620
Sinter Temperature (°C)


bulk density
Bulk Density (gm/cm3)
6
5.95
5.9
5.85
1480
1500
1520
1540
1560
1580
1600
1620
Sinter Temperature (°C)

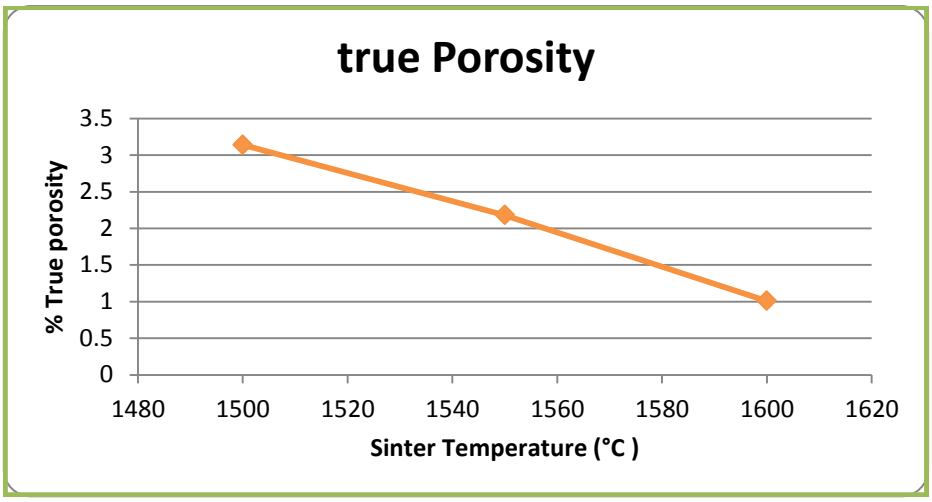


Fig. (1) Schematics of physical tests

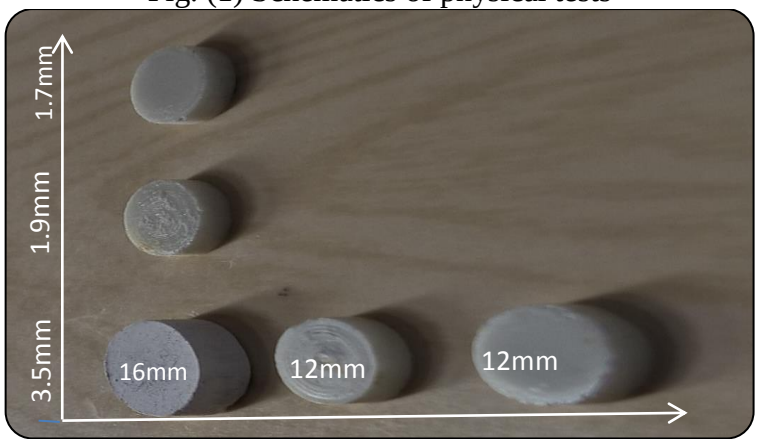


Fig. (2) Sample shape in its three Situation, the vertical side represent the change in the thickness according to the process state [before sintering, after sintering & after grinding], & the horizontal side represent the change in the diameter before and after sintering

3 – 3 Mechanical Tests Results:-

1 - Micro-Hardness – after applied load (100 gm) on sintered samples, it has been noticed that the hardness will increas with increasing sintering temperature, so that tetragonal YSZ have high strength and fracture toughness as compared with YSZ with cubic or monoclinic phase in high amount. Also after sintering the sample have high density with low porosity, as showing in the figure (2).

2 - Fracture Toughness – different loads have been applied to get clear rhombus of indenter prime with suitable crack length and to Specify the toughness of the samples, where 60kg load has been applied on sample sintered at 1500 and 1600°C, is observed that the indent was very distorted and did not appear in clear dimension with many crackes as shown in the figure (4), then it has been gradually minimize the loads from 60 to 4kg to have obvious indent with low deformation and cracks percent around it. At 1, 2, 3kg the indent have low deformation and cracks as shown in the figure, the complete rhombus shape produce at 1kg load with cracks at the rhombus edges. The best value in fracture toughness data was at 1550°C sintering sample, where this values equal approxematly standered values, this indicates that the physical and mechanical properties at this sintering temperature is the best, so that have good grain size with low stress concetration and porosity.

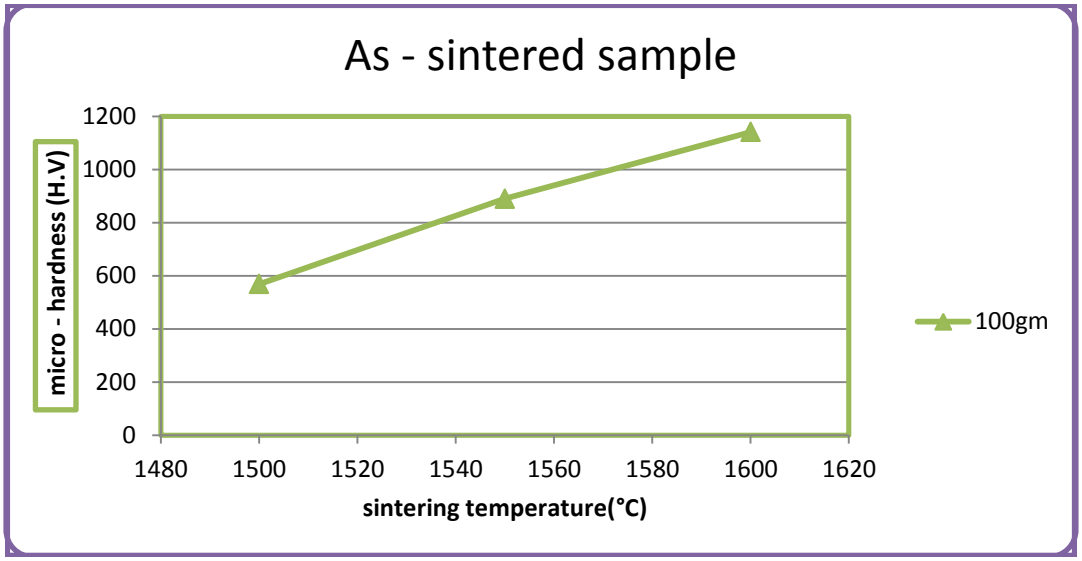


Fig.(2) the relationship between micro-hardness and sintering temperature

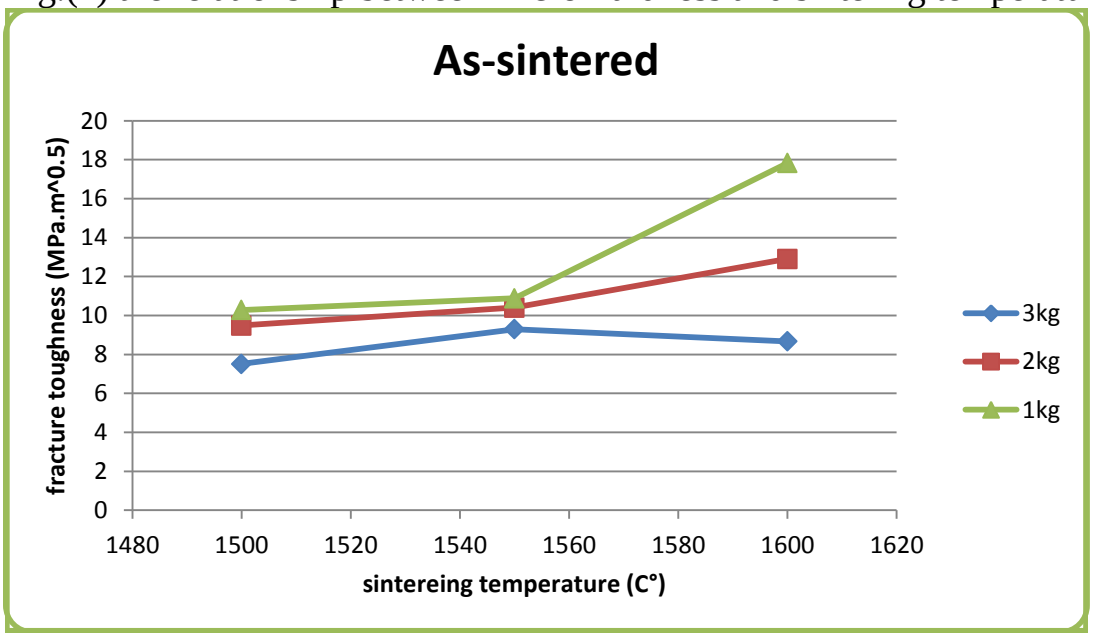
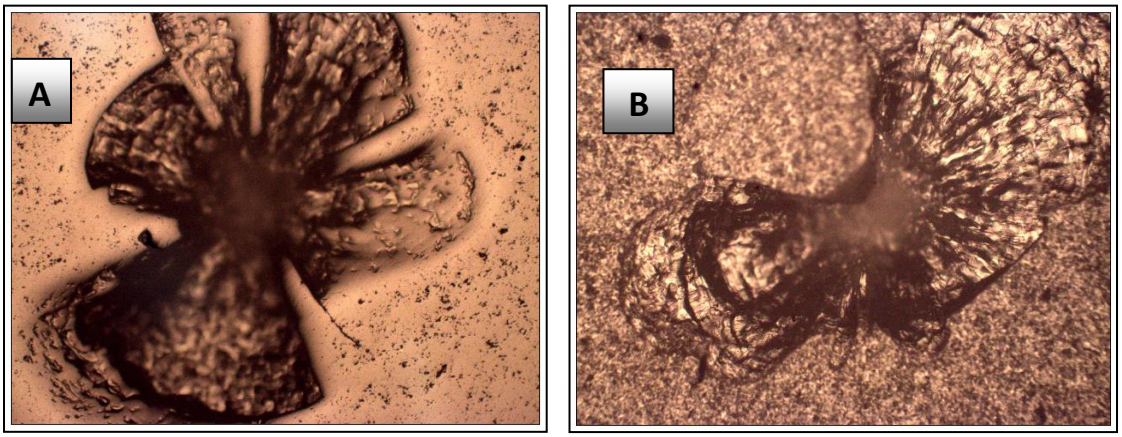
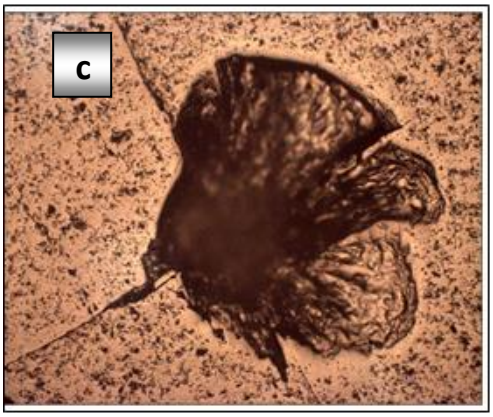
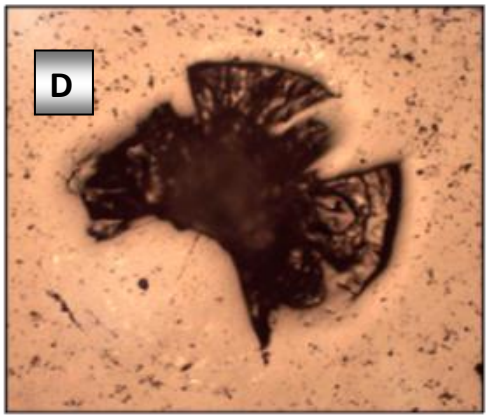


Fig. (3) The relationship between fracture toughness and sintering temperature




C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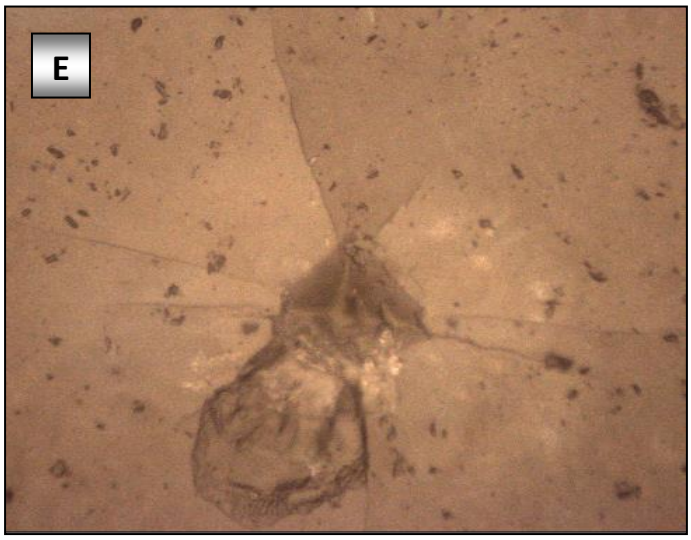
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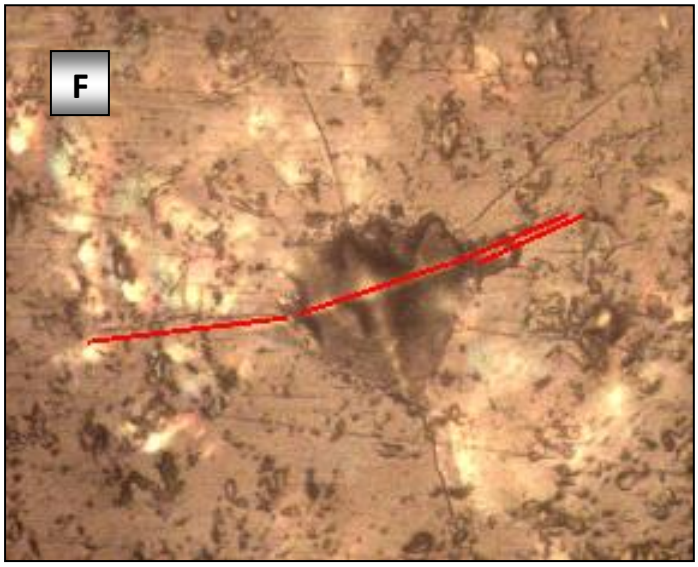
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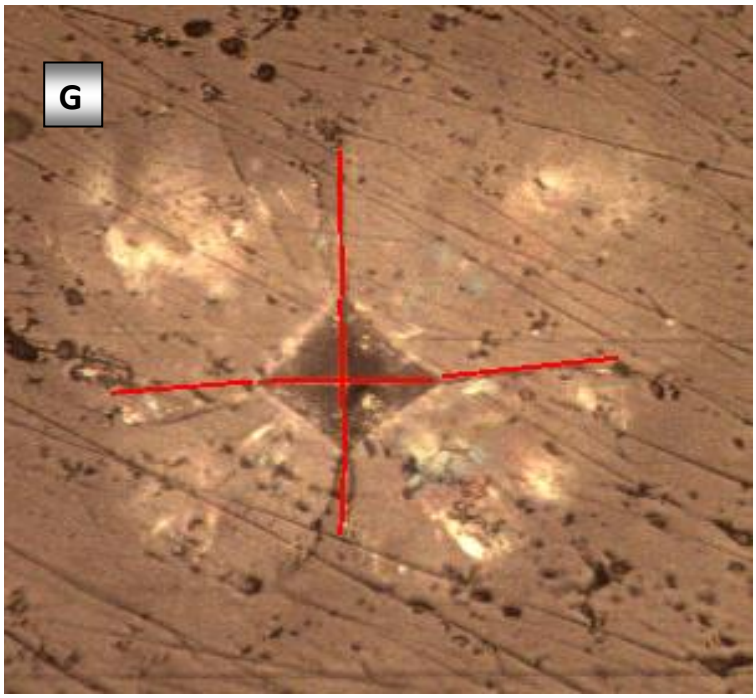
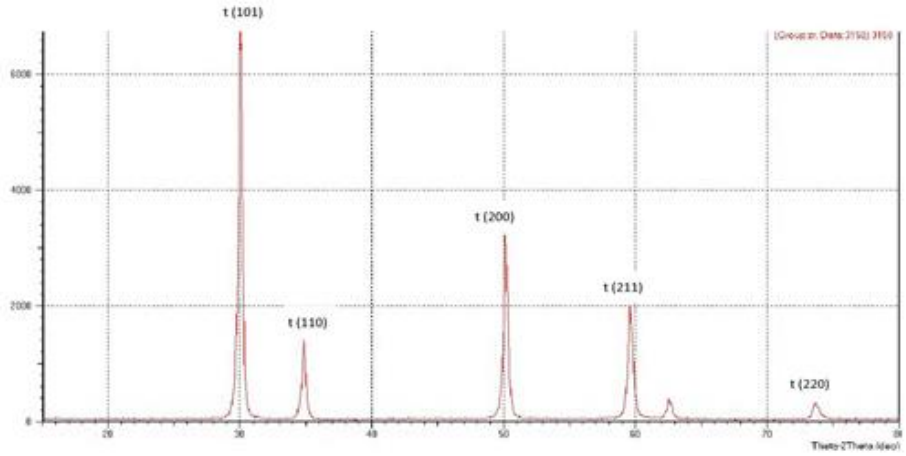


Fig. (4) Vickers indenter for Y-TZP sample sintered at 1600ºC at 10x (A) 60kg load (B) 50kg load (C) 40kg load (D) 30kg load (E) 3Kg load (F)2Kg load (G) 1Kg load

3 – 4 Structural Tests Results:-

1- XRD- the XRD patters of the powder and sintered samples show 100% tetragonal phase present with no monoclinic phase as shown in the figure (5) the XRD chart diagnoses by ICDD card (04-005-4210), where tetragonal phase present in different angles and plans

Figure (6) show the overlay of XRD charts for samples sintered at [1500 – 1550 and 1600ºC] and table (1) show the XRD data for samples at different treatment. It's noticed from the table that the cubic phase Produce after sintering forming duplex structure with tetragonal phase in sintered samples at all sintereing temperature, where the amount of c-phase equal ≅ 10%, 9% and 7% in sample sinterd at 1500, 1550 and 1600ºC. Monoclinic and rhombodral phases produce when samples sintered at 1550 and 1600ºC below detection limits.



When sintering time and temperature increas the diffraction peaks will directed to c-phase, at highest sintering temperature and time even m-phase could be

detected due to spontanous transformation of metastable t-phase into m-phase(Tomaz Kosmac and Andraz Kocjan, 2012) (Masanao Inokoshia and others, 2014). The increas in grain size during sintering will lower tetragonal stability and the possibility of t-phase to form large portion of cubic grains in the material, where its shown that the cubic grains are enriched with yttrium, causing depletion of yttria in the surrounding tetragonal grains (Jerome Chevalier and others, 2004) so as the cubic zirconia increas in sintered ceramic, yttria content of t-phase decrease (Tomaz and Andraz, 2012).

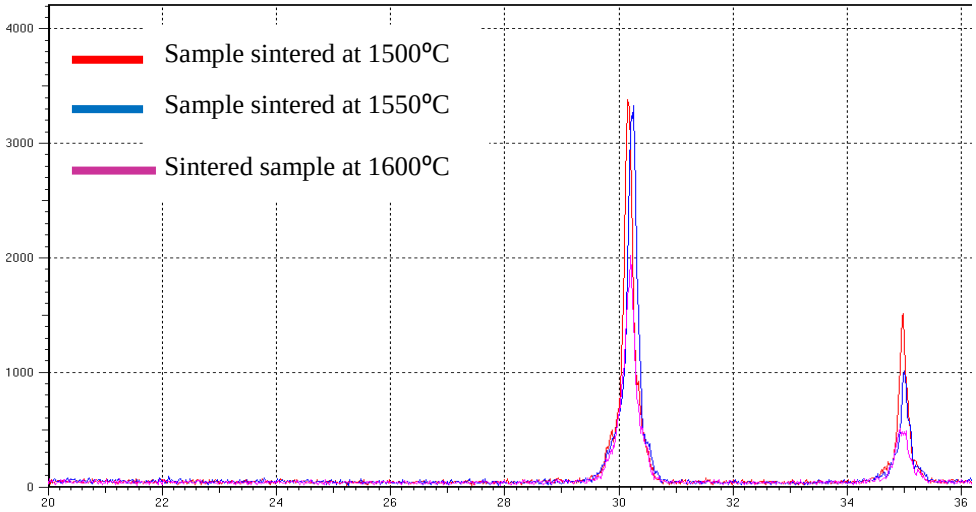


Fig. (6) the overlay of XRD chart for samples at different sintering temperature

Table (1) XRD data of sintered samples

Sintering temperature	2θ	d lattice	h k (l)	I/I_1	Phase type	Card NO.	treatment process
1500°C No.1	34.9912	2.56226	200	29	c	01-089-9069	As-sintered
	72.1207	1.30862	004	5	t	04-005-4210	
	72.5405	1.30207	004	5	t	04-005-4210	
	73.7897	1.28309	400	100	c	01-0890-9069	
1550°C No.6	29.7836	2.99734	101	5	t	04-005-4210	As-sintered
	70.2912	1.33813	-223	5	m	04-013-6620	
	71.2149	1.32302	-104	8	m	04-013-6620	
	72.2206	1.30705	004	2	t	04-005-4210	
	73.7852	1.28320	400	100	c	01-089-9069	
1600°C No.11	34.9672	2.56397	200	30	c	01-089-9069	As-sintered

2 – AFM - AFM was use to follow the chang that present in grain size befor and after sintering, where the results show change in grain size and grain shape after sintering for different sintering temperature specially at $1600C^0$, as shown in the figure (7). Also the results show there is no porosity on the samples surface and this concede Archemids results. Figure (8) shows the granularity accumulation distribution chart of the powder grain size diameter. As showing from the chart the powder have grain size ranging between (85 to 130nm). And the granularity accumulator distribution charts of sintered samples that when sintring temperature increas the grain size diameter increas $D_{powder} < D_{1500^0C} < D_{1550^0C} > D_{1600^0C}$ (i.e. in tetragonal crystal c/a ratio decreas as the temperature increas (W. David Kingery and others, 1976).

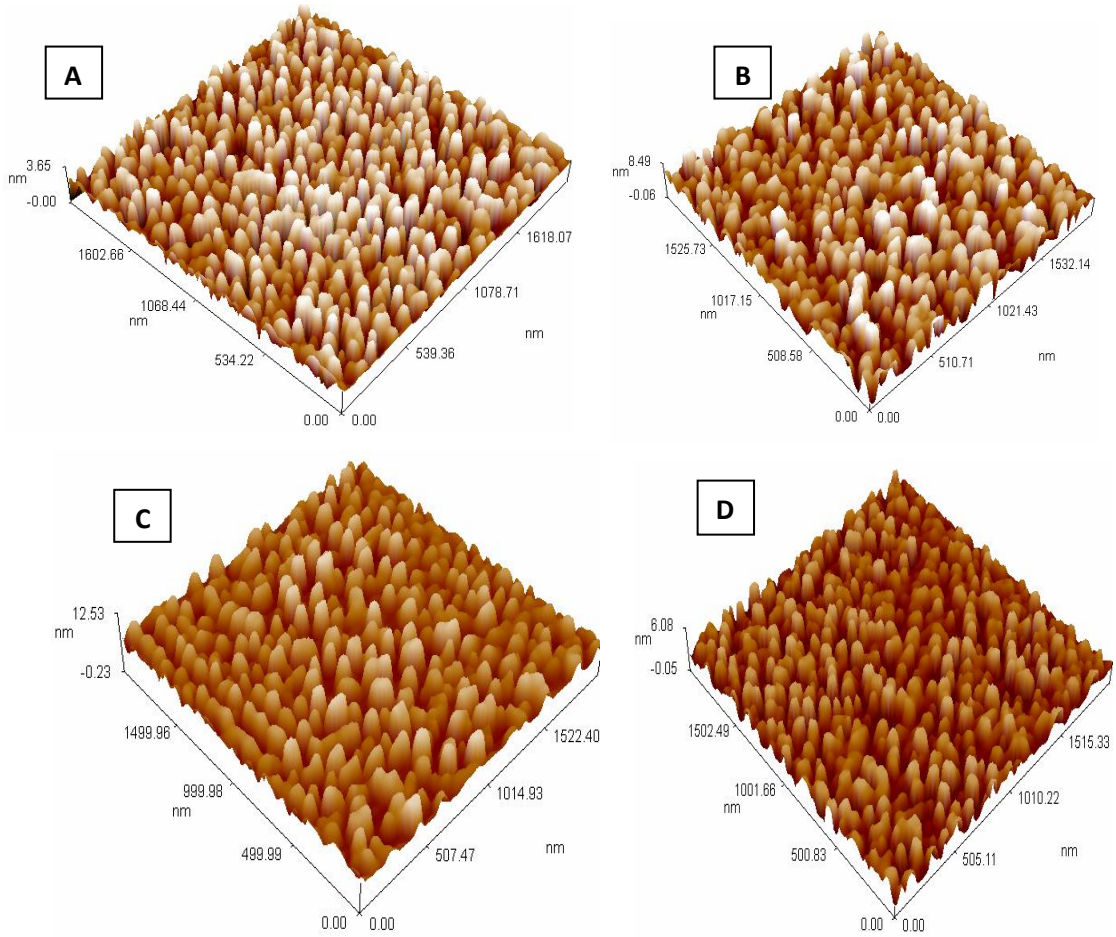
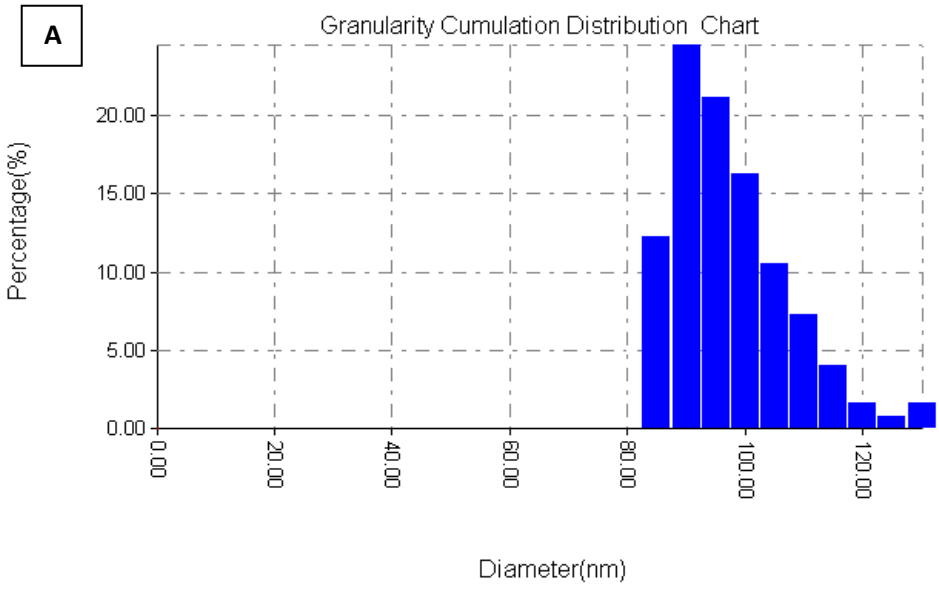


Fig. (7) AFM image for samples (A) powder (B) AS-sintered sample at 1500°C (C) AS-sintered sample at 1550°C (D) As-sintered sample at 1600°C



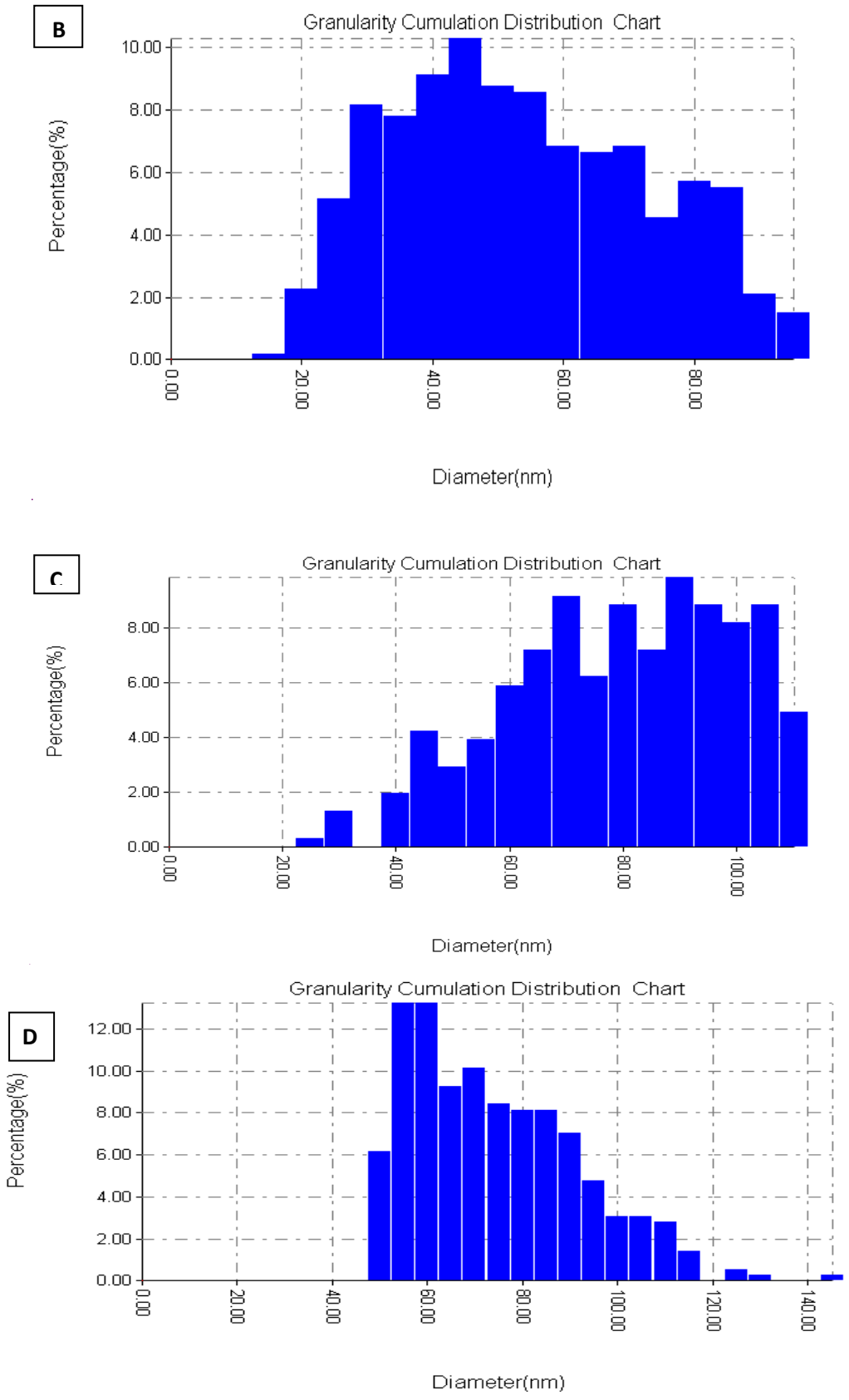


Fig. (7) AFM distribution charts for samples grain size (A) powder sample (B) As-sintered sample at 1500°C (C) As-sintered sample at 1550°C (D) As-sintered sample at 1600°C

3- Micro-Strain - After sintering this heat treatment will produce thermal stresses and this will produce micro-strain in the sintered samples, figure (8) clarifies the relationship between micro-strain with sintering temperature. From the figure its noticed that micro-strain increas in the negative value with increas sintering temperature, where the lattice dimension (d) decreas after sintering, in tetragonal crystal c/a ratio decreases as the temperature increase (W. David Kingery and others, 1976).

The difference in the XRD patterns for sintered samples occurs in the peak width and height and the deflection peaks at the same angle in different chart (the pressure of pressing and thermal treatment produce local stresses and strain between grains at the content point (Yusheng Zhao, and Jianzhong Zhang, 2008).

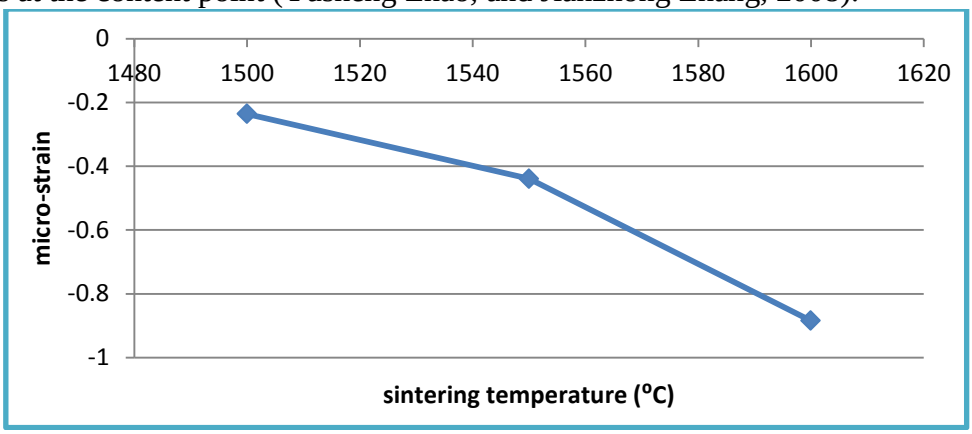
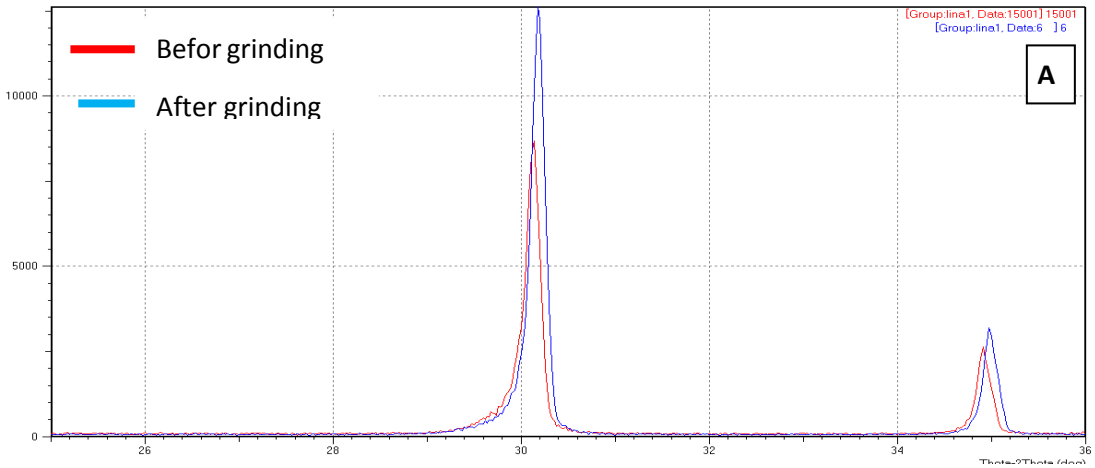


Fig. (8) micro-strain of sintered samples

For micro-hardness and fracture toughness to be tested the samples must be prepared by grinding and polishing process, so XRD test was made to clarify the effect of grinding on the samples. Figure (9) illustrates the effect of grinding on the samples structure. As showing from the figure the peak intensity and width will change after sample grinding (i.e. the change in (d) lattice spacing) but there was no phase transformation occurs, where the residual stresses wasn't enough to produce transformation by induced stresses.



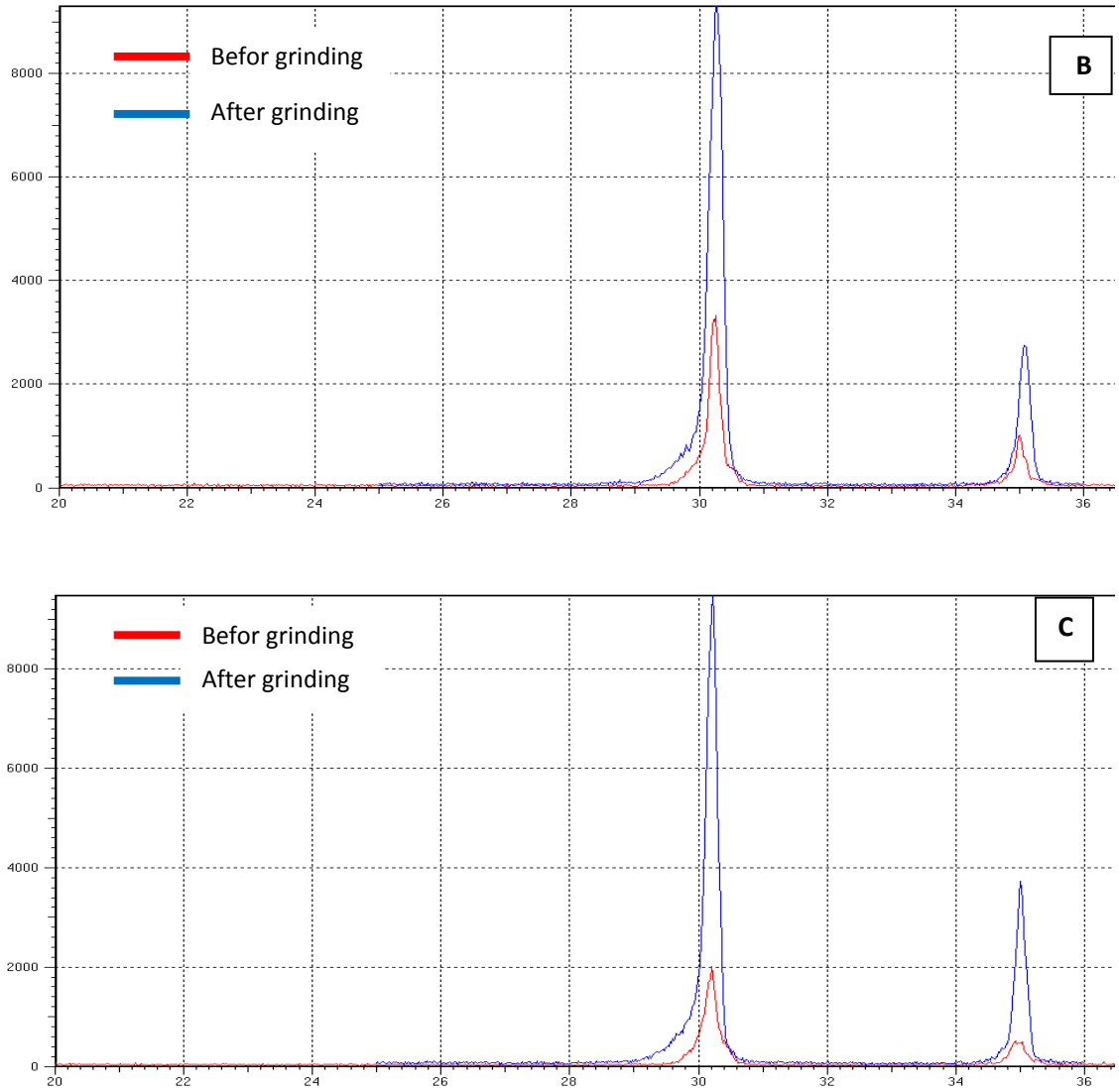


Fig. (9) XRD charts of the samples (A) powder chart (B) overlay of As-sintered samples (C) as-sintered sample at 1500°C chart-befor and after grinding (D) as-sintered sample at 1550°C chart-befor and after grinding (E) as-sintered sample at 1600°C chart-befor and after grinding

4 – Conclusion:-

Based on the results in this research we concluded:

1 – Pressing load has effects on the following processes. There must be suitable percent between pressing load and sample dimension.

2 – Grain size, number and the size of porosity, and micro-strain affected by sintering temperature.

3 – The low percent in mechanical work may be not enough to produce phase transformation but enough to change lattice dimension.

4 – The best results have been taken during mechanical tests for sample sintered at 1550C°.

References

ASM International," Mechanical Testing and Evaluation", published in 2000 as Volume 8, The Volume was prepared under the direction of the ASM Handbook Committee.

Caroline Cotesa, Anelyse Arataa, Renata M. Meloa, Marco A. Bottinoa, João P.B. Machadob, Rodrigo O.A. Souzac,2014, "Effects of aging procedures on the

topographic surface, structural stability, and mechanical strength of a ZrO2-based dental ceramic", *journal of dental materials*, vol. 30, pp.e396–e404.

Enrique Rocha-Rangel," Fracture Toughness Determinations by Means of Indentation Fracture", Universidad Politécnica de Victoria México

Mccolm I.J., Leonard Hill, 1983, "Ceramic science for materials technologists"**.**

Jerome Chevalier,2006, "What future for zirconia as a biomaterial?" Biomaterials 27 ,535–543.

Jerome Chevalier, Sylvain Deville, Etienne M.unch, Romain Jullian, and Frederic Lair , 2004, " Critical Effect Of Cubic Phase On Aging In 3 Mol% Yttria-Stabilized Zirconia Ceramics For Hip Replacement Prosthesis", *Journal of Biomaterials, vol.* 25,pp. 5539–5545.

Karel Maca, Vaclav Pouchly, Pavel Zalud,2010,"Two-Step Sintering of oxide ceramics with various crystal structures", Journal of the European Ceramic Society 30 583–589.

Malaysian standard, fine ceramics,2003, (advanced ceramics, advanced technical ceramics) - determination of density and apparent porosity,(Iso 18754:, idt) .

Manual of weighing applications, part 1- density, marketing, weighing technology, February 1999.

Masanao Inokoshia, Fei Zhang, Jan De Munck, Shunsuke Minakuchi, Ignace Naert, Jozef Vleugels, Bart Van Meerbeek, and Kim Vanmeensel, 2014," Influence Of Sintering Conditions Onlow-Temperature Degradation Of Dental Zirconia", *Journal of dental materials*, vol. 3 0, pp. 669–678.

R.Stevens, 1986, "zirconia and zirconia ceramics", 2nd edition.

Tomaz Kosmac, Andraz Kocjan , 2012, "Ageing of Dental Zirconia Ceramics", *Journal of the European Ceramic Society*, vol. 32, pp. 2613–2622.

David Kingery W., Bowen H. K., Donald R. Uhlmann, January 1976, *Introduction to Ceramics*, Massachusetts Institute of Technology, A Wily Interscience Publication , 2nd Edition.

Yusheng Zhao and Jianzhong Zhang, 2008," Microstrain and grain-size analysis from diffraction peak width and graphical derivation of high pressure thermomechanics", Journal of Applied Crystallography ISSN 0021-889.

Yusheng Zhao, and Jianzhong Zhang,October 2008," Microstrain and grain-size analysis from diffraction peak width and graphical derivation of high pressure Thermomechanics", *Journal of Applied Crystallography*, ISSN 0021-8898, 1.

Khamv Z., Moshiri Z., erdi, 2012, " Zirconia: An Up-to-date Literature - Review", DJH; Vol.4, No.1

جنان ستار خشان، " تاثير اضافة الالومينا على الخواص و البنية الدقيقة لنظام زركونيا ياتريا"، رسالة ماجستير، 2001

samples	
Y-TZP	yttria tetragonal zirconia polycrystalls
AFM	Atomic force microscopy
XRD	X-ray diffraction
t	tetragonal
m	monoclinic
c	cubic
PVA	Poly vinyl alcohol
YSZ	yttria stabilized zirconia
Wd	dry weight
Wi	Immersion weight
Ws	saturated weight

ρ_w	water density
T.P	True porosity
B.D	density of sintered sample
T.D	theoretical density of sintered sample
D_1	diameter after sintering
D_0	diameter before sintering
t_0	thickness before sintering
t_1	thickness after sintering
K_{IC}	Fracture toughness
H	Vickers hardness
P	Test load in Vickers hardener
c	Average length of the cracks obtained in the tips of the Vickers marks
a	Half average length of the diagonal of the Vickers marks
Xm	mol fraction of m-phase
Im	area under curve of m-phase